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Isotopic anomalies in extraterrestrial grains

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Abstract

Isotopic compositions are referred to as anomalous if the isotopic ratios measured cannot be related to the terrestrial (solar) composition of a given element. While small effects close to the resolution of mass spectrometric techniques can have ambiguous origins, the discovery of large isotopic anomalies in inclusions and grains from primitive meteorites suggests that material from distinct sites of stellar nucleosynthesis has been preserved. Refractory inclusions, which are predominantly composed of the refractory oxides of Al, Ca, Ti, and Mg, in chondritic meteorites commonly have excesses in the heaviest isotopes of Ca, Ti, and Cr which are inferred to have been produced in a supernova. Refractory inclusions also contain excess ^{26}Mg from short lived ^{26}Al decay. However, despite the isotopic anomalies indicating the preservation of distinct nucleosynthetic sites, refractory inclusions have been processed in the solar system and are not interstellar grains. Carbon (graphite and diamond) and silicon carbide grains from the same meteorites also have large isotopic anomalies but these phases are not stable in the oxidized solar nebula which suggests that they are presolar and formed in the circumstellar atmospheres of carbon-rich stars. Diamond has a characteristic signature enriched in the lightest and heaviest isotopes of Xe, and graphite shows a wide range in C isotopic compositions. SiC commonly has C and N isotopic signatures which are characteristic of H-burning in the C-N-O cycle in low-mass stars. Heavier elements such as Si, Ti, Xe, Ba, and Nd, carry an isotopic signature of the s-process. A minor population of SiC (known as Grains X, *ca.* 1 %) are distinct in having decay products of short lived isotopes ^{26}Al (now ^{26}Mg), ^{44}Ti (now ^{44}Ca), and ^{49}V (now ^{49}Ti), as well as ^{28}Si excesses which are characteristic of supernova nucleosynthesis. The preservation of these isotopic anomalies allows the examination of detailed nucleosynthetic pathways in stars.

Introduction

The study of isotopic anomalies in meteorites offers a direct image of nucleosynthesis in stars and the processes by which dust is dispersed into the interstellar medium. The solar system is composed of a mixture of a variety of nucleosynthetic sources which were homogenized during the solar nebula and further during planetary formation. Isotopic abundances on Earth are affected only by radioactive decay and by the relatively small fractionations caused by the differences in the masses of the isotopes during kinetic processes. The largest fractionations are found in H (which has the largest mass difference between two isotopes) and fractionation effects become smaller with increasing mass. However, in different nucleosynthetic environments in stars, there are large (orders of magnitude) variations in isotopic production rates. The preservation of material from these distinct environments results in grains with diverse isotopic compositions.

The measurement of isotopic compositions generally involves the measurement of a ratio of one isotope to another in a mass spectrometer. For an element with more than three isotopes, an isotopic composition is said to be anomalous if it cannot be related to the terrestrial (and by inference solar) composition through a mass fractionation law that describes the behaviour of the isotopes in physicochemical processes including the measurement process itself. A mass fractionation correction can be achieved by using one isotopic ratio to determine the fractionation and then removing that degree of fractionation from the other isotopic ratio(s). A fractional deviation of a fractionation-corrected ratio is often reported such that a deviation of zero is normal, positive indicates the ratio exceeds normal and negative indicates it is below normal. For an element with only two isotopes, a mass fractionation correction is not possible and the isotopic ratio is said to be anomalous if it exceeds the range of that ratio typically found on Earth.

A wide variety of mass spectrometers have been used in analyzing isotopic compositions of meteoritic phases. Gas and solid-source mass spectrometers require mutigrain samples to achieve sufficient signal for a precise analysis but have clearly characterized various mineralogical grain types (diamond, silicon carbide, graphite) as highly anomalous. But perhaps the most telling information is coming from ion microprobe analysis which allows the measurement of single grains (to submicron sizes) for a number of elements and isotopic systems which can then be related to distinct astrophysical settings.

This paper gives a brief introduction to nucleosynthesis in stars, gives an overview of some of the isotopically anomalous extraterrestrial grains found so far, and relates these to some distinct astrophysical settings which are possible sites for grain formation. It is not intended to be comprehensive review of all knowledge of the isotopic systematics of extraterrestrial grains but has been written to give a more general outline of the field along

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with some illustrative examples. More detailed reviews and information can be found in Lee (1988) and Clayton *et al.* (1988) for isotopic systematics of refractory inclusions, and Anders & Zinner (1993) and Ott (1993) for interstellar grains. The role of ion microprobe mass spectrometry in these fields has been reviewed by Ireland (1995).

Nucleosynthesis

Apart from ^{1}H, ^{2}H, ^{3}He, ^{4}He and ^{7}Li which were formed in Big Bang nucleosynthesis, all other nuclides were produced, and are being produced, in nuclear reactions predominantly in stars, but also in circumstellar environments and the interstellar medium. In light of the abundance curve of the nuclides (Fig 1), Burbidge *et al.* (1957) specified 8 modes of nucleosynthesis that could account for its features. The two fundamental thermonuclear reactions driving stars are *H-burning* and *He-burning*. Upon exhaustion of the H, the star contracts under its own gravity and if the star has sufficient mass, He will ignite and burn to form C and O. Reactions involving the successive addition of α particles (*α-process*) to nuclei heavier than ^{20}Ne result in four-structure nuclei (^{24}Mg, ^{28}Si, ^{32}S, ^{36}Ar, ^{40}Ca, and possibly ^{44}Ca) at higher abundances than their neighbours. For a massive star, nucleosynthesis can proceed up to the mass region of the iron group of elements where the nuclear binding energy is at a maximum per nucleon and no further energy can be released by fusion. At this stage, nuclear statistical equilibrium (*e-process*) is achieved in the reactions and leads to a build-up of Fe-group-element abundances. The low-abundance nuclides ^{6}Li, ^{9}Be, and ^{10}B and ^{11}B are unstable in stellar interiors and require formation in low temperature environments. The formation of these elements was assigned to the *x-process* (x for unknown) which is probably largely due to spallation. Burbidge *et al.* (1957) also used the x-process to explain the abundance of D, but this is now assigned to the Big Bang.

Elements heavier than the Fe group are mainly produced in neutron-capture reactions. In the *s-process*, the addition of neutrons is slow relative to the likelihood of a β decay, whereas in the *r-process* the addition of neutrons happens on a rapid time-scale and very neutron-rich nuclei can result. The s-process occurs in asymptotic giant branch (AGB) stars undergoing core He burning where neutrons are released through reactions such as ^{13}C(α,n)^{16}O or ^{22}Ne(α,n)^{25}Mg. The r-process requires a large neutron flux and it is likely to be related to supernovae. Low abundance nuclei on the low mass side of the valley of stability (*i.e.* neutron-poor isotopes) are referred to as *p-process* nuclides and these have probably formed by photonuclear reactions, also in supernovae.

A supernova of Type II occurs when a massive star has consumed most of its nuclear fuel. At this stage it has an Fe-rich core and is surrounded by layers still burning the remnants of its fuel. Upon near exhaustion of this fuel, the star can no longer support itself gravitationally and it implodes. The rebound shock wave ejects the outer layers while the material inside the mass cut collapses into a degenerate neutron star or pulsar. Novae and supernovae of Type I involve binary stars with a white dwarf left after the AGB phase. A nova can occur if the white dwarf accretes more than 10^{-3} solar masses of H from its companion resulting in explosive H burning. If the accreting white dwarf eventually exceeds the Chandrasekhar limit (1.4 M_{solar}) then the star collapses and explodes as a Type Ia supernova.

The evolution and ultimate state of a star is governed primarily by two parameters, metallicity and mass. The metallicity of a star is the proportion of elements heavier than H and He and it affects nucleosynthesis in that heavier elements can act as seeds for more energetic reactions. The mass of the star limits the ultimate temperature and pressure in the stellar core. For a star less than

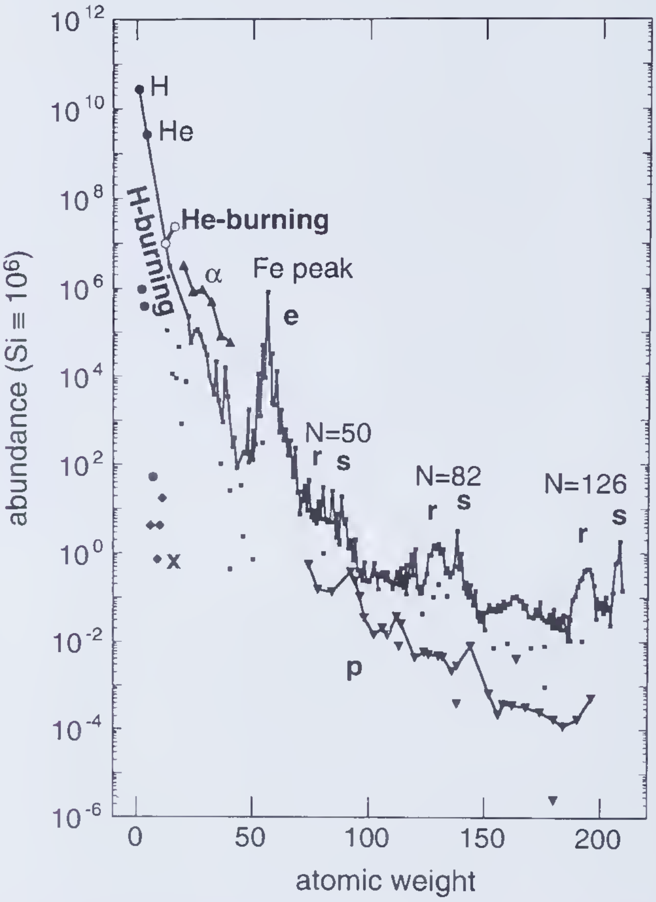

Figure 1. The solar abundances are an average of a number of different nucleosynthetic sites. Burbidge *et al.* (1957) first described the features of the nuclidic abundance curve in terms of eight discrete stellar processes and with only a little refinement the principal tenants are still applicable. *H-Burning* and *He-burning* are the fundamental thermonuclear reactions driving stars converting H to He and He to C and O. The relatively high abundances of nuclei in the mass range 20 - 40 with mass numbers divisible by 4 (*i.e.* ^{20}Ne, ^{24}Mg, ^{28}Si, ^{32}S, ^{36}Ar, ^{40}Ca) are due to progressive addition of α-particles (*α-process*). Stars more massive than 9 M_{solar} can ignite the C,O-rich core left after He burning and for the most massive stars nucleosynthesis can proceed to equilibrium burning (*e-process*) at the iron abundance peak. The s- and r-processes refer to progressive addition of neutrons at slow (*s-process*) and rapid (*r-process*) rates with respect to the competing β decays. Note the peaks in abundance of s- and r-process nuclei around magic number nuclei (N=50, 82, and 126). Low-abundance neutron-poor nuclei are likely due to photonuclear reactions (*p-process*). Finally the abundances of the light, low-abundance elements Li, Be, B as well as D, were attributed to an unknown process (*x-process*). Deuterium is now attributed to Big Bang production and the abundances of Li, Be, and B are likely from spallation of heavier nuclei.

9 M_{solar}, no nucleosynthesis beyond He-burning occurs and the star decays into a white dwarf. Heavier stars can ignite the C-O core and reactions proceed to build heavier nuclei (up to ^{56}Fe) with the heaviest stars eventually exploding in Type II supernovae. In the chemical evolution of the galaxy, material is ejected from a dying star to become available for the next generation. Supernovae are extremely efficient at getting a large mass of matter into the interstellar medium, but these events are uncommon since they only occur in the heaviest stars (1 event per 50 years per galaxy producing 2 M_{solar} = 0.04 $M_{solar}yr^{-1}$). Most material ejected into the interstellar medium comes from the winds of AGB stars and ensuing planetary nebula (1 yr^{-1} producing 0.3 M_{solar} = 0.3 $M_{solar}yr^{-1}$). Novae are more frequent but produce far less material (30 yr^{-1} producing 10^{-4} M_{solar} = 0.003 $M_{solar}yr^{-1}$; Truran 1993).

Winds carry material away from the star surface into the circumstellar environment where it condenses into grains, and these grains continue to move away from the star and may be entrained into molecular clouds to form the next generation of stars. In this way, our solar system was formed in a molecular cloud that had contributions from a large number of stars of different generations.

Isotopic anomalies

Isotopic anomalies were first discovered for the noble gases Ne and Xe from chondritic meteorites (Reynolds & Turner 1964; Black & Pepin 1969). However, the systematics of the noble gases were poorly understood and an origin from within the solar system from radiogenic decay of transuranic nuclides and fission could not be dismissed. Furthermore, in the 1960s the current paradigm on the evolution of the solar nebula was that it attained sufficiently high temperatures to volatilize most if not all of the interstellar dust falling into it and therefore all isotopic heterogeneity had been removed (Cameron 1962). The discovery of isotopic variations in O, the most abundant lithophile element in the solar system quickly changed the situation (Clayton *et al.* 1973).

Refractory Inclusions

The oxygen anomalies, excesses in ^{16}O of up to 5 %, were discovered in refractory inclusions from the Allende carbonaceous chondrite. These inclusions are composed of refractory oxides that would condense from a cooling gas of solar composition, and the Allende inclusions commonly include the minerals spinel $MgAl_2O_4$, melilite $Ca_2Al_2SiO_7$ - $Ca_2MgSi_2O_7$, pyroxene $CaMgSi_2O_6$, and perovskite $CaTiO_3$. Refractory trace elements are enriched in these inclusions at approximately 20 times that found in bulk carbonaceous chondrites indicating that the refractory inclusions could have condensed as the first 5 % of solar material. These characteristics suggested that refractory inclusions would be the best place for a search for isotopic anomalies since these early-formed solids may have crystallized before all isotopic heterogeneities were removed from the solar nebula.

With the discovery of oxygen isotopic anomalies, the race was on to find further isotopic effects. Magnesium isotopic abundances were found to give excesses and deficits in ^{26}Mg after correcting for mass-dependent fractionation (Gray & Compston 1974; Lee & Papanastassiou 1974), but large excesses of ^{26}Mg which were correlated with Al/Mg in a number of phases from a single refractory inclusion established the presence of short lived ^{26}Al in the early solar system (Lee *et al.* 1977). Excess ^{26}Mg (*i.e.* extinct ^{26}Al) is commonly present in refractory inclusions at a maximum level of 5 10^{-5} ^{27}Al.

During the final stages of hydrostatic burning in a massive star, the Fe-group elements form under quasi-equilibrium conditions since binding energy per nucleon is at a maximum. However, during the supernova the isotopic compositions of the Fe group elements could be affected by large changes in the physical conditions of nucleosynthesis. Furthermore, titanium, on the wing of the Fe abundance peak, is highly refractory and concentrated in the inclusions. Titanium isotopic anomalies were first discovered as a 0.1 %, or 1 ‰, enhancement in ^{50}Ti, a very small effect barely resolvable at that time (Heydegger *et al.* 1979). Soon, however, titanium isotopic anomalies became regarded as being ubiquitous in refractory inclusions (Niemeyer & Lugmair, 1981). Further developments in mass spectrometry revealed effects in other Fe-group elements including excesses of ^{48}Ca (Jungck *et al.* 1984), and ^{54}Cr (Birck & Allègre, 1984). The common feature of these anomalies is that they occur in the heaviest nuclides of each element and hence suggest a common nucleosynthetic component is responsible. These excesses in ^{48}Ca, ^{50}Ti, and ^{54}Cr were successfully modelled as the products of explosive nucleosynthesis around a supernova whereby reactions in the ejecta resulted in neutron-rich compositions (Hartmann *et al.* 1985). Coincidentally, a supernova had earlier been proposed not only as the source for ^{16}O and ^{26}Al but also as a trigger for the collapse of the molecular cloud into the solar system (Cameron & Truran 1977).

Refractory inclusions are also found in other meteorites besides Allende, and in particular the refractory inclusions of CM meteorites such as Murchison and Murray contain corundum Al_2O_3 and hibonite $CaAl_{12}O_{19}$. The presence of these minerals with even higher condensation temperatures than the assemblages of the Allende inclusions suggested that these might contain even larger isotopic anomalies. However, the CM inclusions were very small, seldom over 0.2 mm. The mass spectrometry of the Allende inclusions involved chemical separation of the elements of interest and then loading the separate onto a filament which was heated to a temperature sufficient to ionize the element. With such small samples from Murchison, the prospect of conventional thermal ionization mass spectrometry was not good. However, ion microprobes were beginning to be utilized in the search for isotopic anomalies and the small CM inclusions were an ideal place to start. The ion microprobe utilizes a focussed primary beam of O^- or Cs^+ ions to sputter away the sample. Sputtering with an energetic ion beam results in a small fraction of the ejected atoms being ionized and these can be extracted and passed to a mass analyzer. The benefit of ion probe analysis is that a single inclusion can be analyzed for a

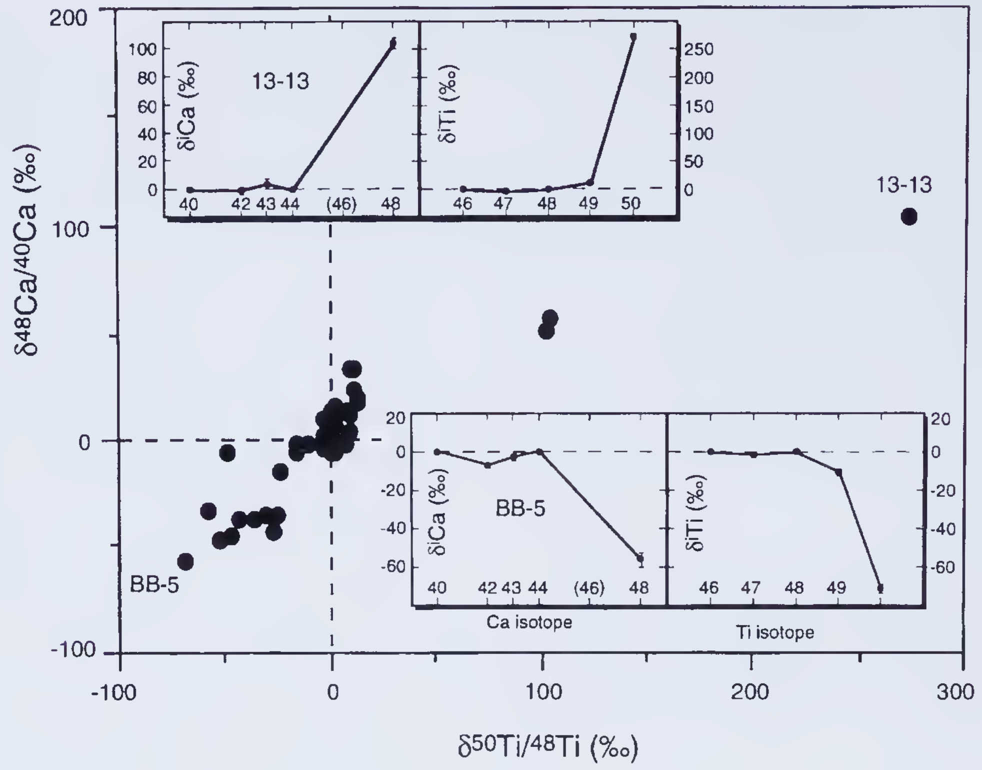

Figure 2. Ca and Ti isotopic compositions in hibonite $(Ca[AlMgTi]_{12}O_{19})$ inclusions display a large range from excesses in the most neutron rich isotopes to deficits while the other isotopes are close to solar proportions (defined as deviations, δ^{i}Ca or δ^{i}Ti, in ‰). The most anomalous grains are both from the Murchison meteorite, 13-13 (Ireland 1990) and BB-5 (Hinton *et al.* 1987) which have large excesses and large depletions respectively in ^{48}Ca and ^{50}Ti (insets). The ^{48}Ca and ^{50}Ti anomalies are clearly correlated and are inferred to come from neutron-rich supernova ejecta.

variety of elements while maintaining the petrographic context.

Titanium isotopic analyses of hibonite-bearing inclusions quickly established the highly anomalous characteristics of these grains (Fahey *et al.* 1985; Ireland *et al.* 1985; Hinton *et al.* 1987) with anomalies more than an order of magnitude larger than those found in Allende. Both excesses and deficits were discovered in ^{50}Ti, and the excesses or deficits in ^{50}Ti were correlated with ^{48}Ca (Fig 2; Zinner *et al.* 1986; Ireland 1990). While the excesses in these isotopes are consistent with the addition of neutron-rich material, deficits are not so readily interpretable. Hinton et al. (1987) proposed that the deficits were due to the solar system being initially depleted in these neutron-rich isotopes and that the solar system received a late injection of supernova ejecta which included ^{16}O and ^{26}Al. However, oxygen isotopic analyses revealed that all hibonite inclusions were enriched in ^{16}O relative to terrestrial by 4 to 7 % (Fahey *et al.* 1987; Ireland *et al.* 1992) precluding a scenario that includes a solar system initially depleted in ^{16}O. Magnesium isotopic compositions of the hibonite grains were split between inclusions that have ^{26}Al/^{27}Al at the canonical solar system value of 5 10^{-5} and inclusions that were below 10^{-5}.

Surprisingly, a number of morphological, chemical, and isotopic features are found to be correlated in Murchison refractory inclusions. Most of the hibonite inclusions can be divided into two types, single hibonite crystal fragments with low TiO_2 concentrations (<2.5 wt%), and hibonite-spinel inclusions with high TiO_2 concentrations (3 - 9 wt%). Most of the crystal fragments show smooth REE patterns with depletions in the more volatile REE Eu and Yb while the spinel hibonite inclusions most commonly have ultrarefractory-REE-depleted patterns. Besides the clear correlation in ^{48}Ca and ^{50}Ti anomalies, it has been noted (Clayton *et al.* 1988) that no inclusion with a large ^{50}Ti anomaly also has excess ^{26}Mg (at 5 10^{-5}), and those inclusions that have anomalies in the ultrarefractory elements of their REE patterns do have excess ^{26}Mg unless they have a Ti isotopic anomaly (Ireland 1990). These correlations and associations clearly indicate that nucleosynthetic anomalies have survived through discrete inclusion-forming events in the early solar system.

But, despite containing isotopically anomalous material, refractory inclusions are not interstellar grains. They are too large and do not preserve the effects expected of solids exposed to travel in the interstellar medium.

Presolar carbon and carbides

The progressive isolation of isotopically distinct noble gas components finally led to the isolation of presolar grains in the laboratory (Fig 3). The main processing involves the acid dissolution of solar system material with further concentration based on other physical properties such as density. It is therefore no surprise that the first interstellar grains identified are all carbon compounds that are resistant to acid attack. These compounds are inferred to be of presolar origin because carbon compounds such as diamond, graphite, and SiC are unstable in the solar nebula and the grains contain material that is isotopically anomalous in the extreme.

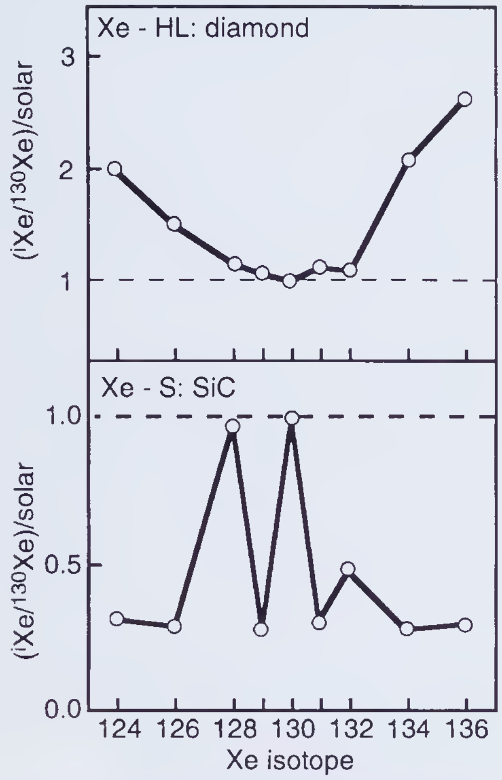

Figure 3. Progressive enrichment of these isotopically exotic Xe components led to the discovery of interstellar diamond and SiC. Interstellar graphite was discovered through isolation of a nearly pure component of ^{22}Ne. The light and heavy components of Xe-HL cannot be produced in the same nucleosynthetic event and are probably the result of mixing (Huss & Lewis 1994). The Xe-S component from SiC reflects a mixture between the composition produced in s-process nucleosynthesis and a near-normal component (Lewis *et al.* 1994).

Diamond was the first type of presolar grain recognized and has the highest abundance at 400 ppm by weight of bulk meteorite (Lewis *et al.* 1987). The diamonds have an average size of only 2 nm and a characteristic enrichment of the heavy and light isotopes of Xe (Fig 3). The small size of the diamonds means that the individual grains contain only a few hundred atoms and the chemical properties are dominated by the bonds on the surface (Bernatowicz *et al.* 1990). It remains unclear as to how the Xe atoms are located in the diamonds but the concentration levels require that there be only one Xe atom per million diamond grains. One mechanism proposed involves ion implantation of the Xe atoms, but the low concentrations of other elements neighbouring Xe in the periodic table is contrary to that expected. The exact formation environment/mechanism of the diamonds remains enigmatic. The diamonds may have been produced in shock waves from supernovae passing through molecular clouds or from chemical vapour deposition because the free energy difference between diamond and graphite is only 1kcal/mol. Support for this theory comes from the near-normal ^{13}C/^{12}C ratios in the diamonds (Fig 4), although a much larger amount of graphite should have been preserved in the meteorites in these scenarios.

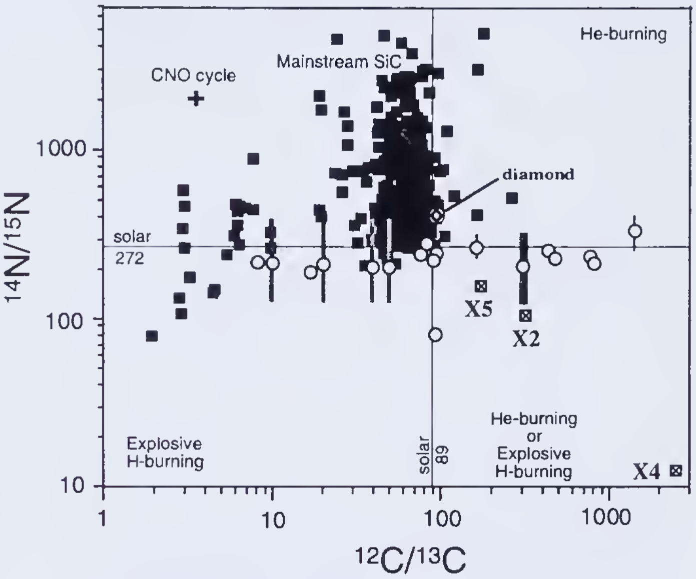

Figure 4. C and N isotopic compositions of presolar diamond, graphite, and silicon carbide. The range of C and N isotopic compositions from these grains is so large that the data is displayed on a plot of the logarithm of the ratios. Diamond has a composition close to solar (origin), while silicon carbide (squares) and graphite (open circles) show large variations. Most SiC occurs in the CNO-cycle quadrant but a suite of grains known as Grains X, which comprise *ca.* 1 % of SiC analyzed, have highly unusual characteristics and are plotted with a crossed square. These Grains X have other unusual isotopic characteristics as shown in Figures 5 and 6. Data from Hoppe *et al.* (1994) and Amari *et al.* (1990).

Silicon carbide was first identified from the Murray CM meteorite by Bernatowicz *et al.* (1987). It is perhaps the most fruitful of the presolar grains since it contains reasonably high concentrations of a number of trace elements and is still reasonably abundant (≈ 6 ppm). Individual grains range in size from <0.2 to around 20 µm allowing ion microprobe analysis of single grains for a variety of elements (see for example Hoppe *et al.* 1994). Ion microprobe analysis of both individual grains and bulk SiC indicated large isotopic anomalies in a number of elements, *e.g.* Si, C, N, Mg, Ti, Ba, Nd, and Sm (Bernatowicz *et al.* 1987; Ireland *et al.* 1991; Zinner *et al.* 1987, 1989, 1991a,b). The mainstream SiC grains show ^{12}C and ^{15}N enrichments (Fig 4) consistent with a mixture of CNO-cycle material with isotopically normal C and N. Most of the heavier elements analyzed from SiC qualitatively show the effects of the s-process with Si isotopic compositions enriched in ^{29}Si and ^{30}Si (Fig 5), Ti isotopic compositions enriched in the minor isotopes relative to ^{48}Ti (Fig 6), and s-process enrichments in heavier elements such as Xe (Fig 3), Ba, Nd, and Sm. These grains are likely to have formed around C-rich AGB stars and dispersed into the interstellar medium by the strong outflows from these stars. However, there are discrepancies in detail between the predicted and measured abundances. For example, the best-fit line passing through the mainstream SiC Si-isotope data has a slope of 1.3 (Fig 5) which differs from the theoretical value of *ca.* 0.35 for s-process nucleosynthesis.

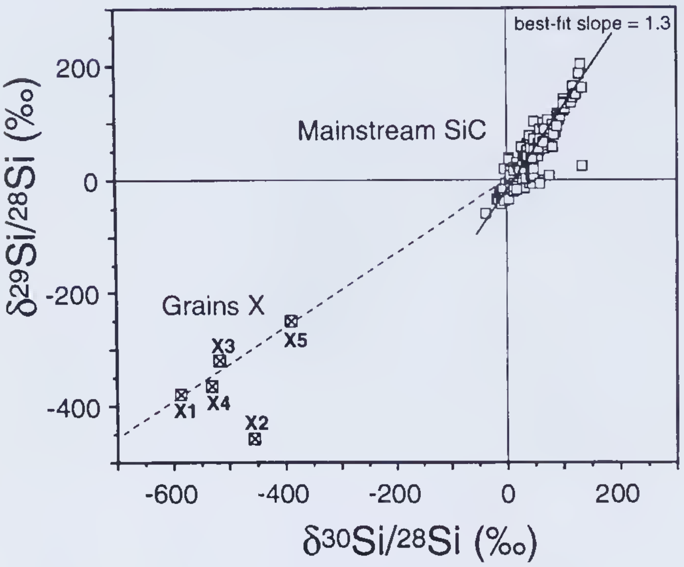

Figure 5. Si isotopic compositions of SiC grains. Most grains show elevated ^{29}Si/^{28}Si and ^{30}Si/^{28}Si ratios relative to terrestrial by up to 200 ‰. The enrichment of ^{29}Si and ^{30}Si can be ascribed to an s-process however the correlation in the ^{29}Si/^{28}Si and ^{30}Si/^{28}Si ratios indicates a slope of 1.3 which does not agree with the predicted value of 0.35 for s-process nucleosynthesis. Grains X have ^{29}Si/^{28}Si and ^{30}Si/^{28}Si ratios below terrestrial (negative delta values) and are inferred to have elevated ^{28}Si abundances which is characteristic of formation in supernova ejecta. Data from Hoppe *et al.* (1994).

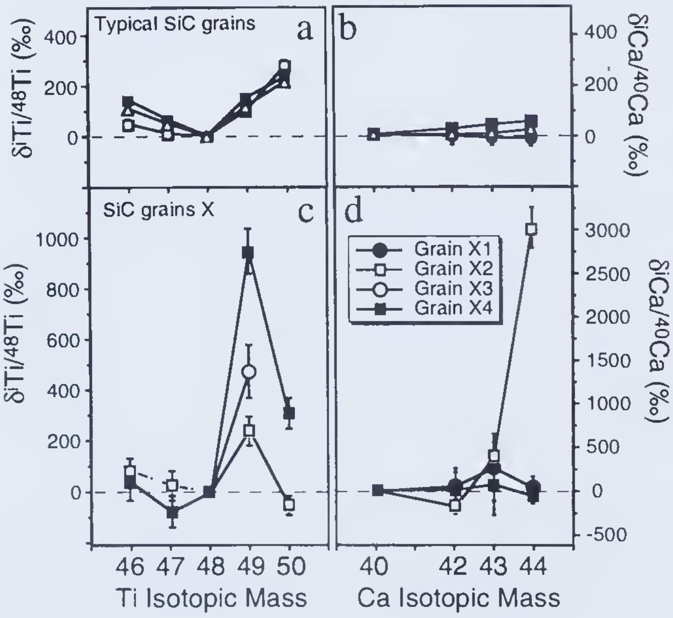

Figure 6. Ca and Ti isotopic compositions in SiC. Mainstream SiC grains have Ti isotopic compositions (a) that show enrichments in all isotopes relative to ^{48}Ti producing a characteristic V-shaped pattern. Ca isotopic compositions of mainstream SiC (b) show no large non-linear effects. Grains X on the other hand, have Ti isotopic compositions enriched in ^{49}Ti and one grain shows a large enrichment of ^{44}Ca. These anomalies are inferred to be due to the decay of ^{49}V and ^{44}Ti which are produced only in supernovae. Data from Ireland *et al.* (1991), Amari *et al.* (1992), and unpublished observations.

A minor fraction of the SiC grains (*ca.* 1 %) show ^{13}C and ^{14}N enrichments as well as excesses of the decay products of short-lived radionuclides (Fig 6) such as ^{26}Al (now ^{26}Mg), ^{44}Ti (now ^{44}Ca), and ^{49}V (now ^{49}Ti). It appears that these short-lived nuclides are only produced together in supernovae and so Grains X may represent material from the C-rich zones in the outer layers of a presupernova star (Amari *et al.* 1992).

Graphite represents less than 2 ppm (by wt) of meteorite and of this material only a fraction is isotopically anomalous (Amari *et al.* 1990). Graphite spherules (1 to 10 µm in diameter) show a similar extreme range in C isotopic compositions as that found for SiC, but isotopically light compositions are more commonly found. Nitrogen is only present at very low levels (*c.f.* nearly 1 % in SiC) and so the lack of large anomalies in this element may not reflect the intrinsic composition. The graphite structure does not allow trace-element substitution to the same degree as SiC but the graphite spherules have been found to contain very small inclusions of refractory carbides of elements such as Si, Ti, Zr, Mo, and W (Bernatowicz *et al.* 1991). It is interesting to note that production of Zr, in particular, is characteristic of the s-process suggesting that at least a fraction of the graphite grains also come from AGB stars.

Interstellar oxides

The isolation of presolar carbon-bearing compounds was aided by their resistance to acid attack and so destruction of all the silicates and oxides in the meteorites leads to increasing concentration of these grains. However, our solar system is clearly not derived predominantly from C-rich stars but has a predominantly O-rich parentage. Most interstellar grains coming into the solar nebula must therefore be oxides but their isolation requires separation from isotopically normal solar nebula oxides which have largely the same physical properties. Nevertheless, interstellar corundum grains have been identified using similar techniques to those used in the isolation of the carbides (Hutcheon *et al.* 1994). Several grains with extreme enrichments of ^{26}Mg and ^{17}O and s-process Ti anomalies have been discovered, suggesting a source from O-rich AGB stars. However, the abundance of the corundum grains is far lower than the carbon-bearing grains suggesting that the dust in the solar nebula was predominantly in the form of silicate rather than oxide.

The stars revisited

Isotopic anomalies direct from the sites of stellar nucleosynthesis are preserved in solar system materials. Refractory inclusions preserve their isotopic anomalies despite being processed in the solar nebula, but both the chemistry and isotopic systematics of carbide grains suggest that they have presolar connections. Local chemical fluctuations allowing carbon or carbides to condense could be envisaged in the solar nebula and so their chemical instability, while supporting an exotic origin, does not preclude formation in the solar system. However, the presence of extreme isotopic anomalies in the presolar grains is the strongest indicator that they have a stellar parentage not related to our Sun. Moreover, the ^{13}C/^{12}C ratios measured from SiC and graphite show a similar range and abundance pattern to that measured in carbon stars (see Anders & Zinner 1993).

Matching isotopic characteristics with a certain class of star is not straightforward, nor in general does a unique classification become apparent. Clearly, interstellar grains must be derived from stars with strong outflow winds or that have undergone some form of explosion to distribute material into the interstellar medium. The main contributor to the SiC and graphite abundances appears to be AGB stars. Perhaps this is not surprising since these stars are common, have strong outflow winds, and hence contribute a large amount of material to the interstellar medium. A small fraction of the SiC grains appears to have been produced in a supernova. It also appears that Fe-group anomalies in refractory inclusions can be related to supernova nucleosynthesis but their isotopic characteristics appear quite different to those in the Grains X. Specifically, Ti from refractory inclusions is anomalous in ^{50}Ti (and to a lesser extent ^{49}Ti) which is related to a neutron-rich equilibrium process. On the other hand, Ti in grains X has a smooth pattern except for ^{49}Ti anomalies that are related to ^{49}V decay. Thus, Ti in the refractory inclusions appears to come from close to the mass cut of a supernova while Ti in Grains X is probably derived from the outer layers of a supernova.

A range of nucleosynthetic sites is now available for study in the laboratory and detailed nucleosynthetic calculations can now be compared with actual compositions. In large part, the agreement is quite acceptable at least qualitatively. For example, the predicted s-process compositions of the elements Xe, Ba, and Nd is in good agreement with the theoretical production. There are differences however that cannot be explained at the present time such as the slope of the Si correlation and the correlation between Si and Ti isotopes in mainstream SiC. Measurements of a wider range of elements and refinement of calculations will hopefully yield better insights into the nucleosynthetic conditions and evolution of stars responsible for the presolar dust grains.

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References

Amari S, Anders E, Virag A & Zinner E 1990 Interstellar graphite in meteorites. Nature 345:238-240.

Amari S, Hoppe P, Zinner E & Lewis R S 1992 Interstellar SiC with unusual isotopic compositions: grains from a supernova? Astrophysical Journal 394:L43-L46.

Anders E & Zinner E 1993 Interstellar grains in primitive meteorites: diamond, silicon carbide, and graphite. Meteoritics 28:490-514.

Bernatowicz T, Fraundorf G, Tang M, Anders E, Wopenka B, Zinner E & Fraundorf P 1987 Evidence for interstellar SiC in the Murray carbonaceous chondrite. Nature 330:728-730.

Bernatowicz T J, Gibbons P & Lewis R S 1990 Electron energy loss spectrometry of interstellar diamonds. Astrophysical Journal 359:246-255.

Bernatowicz T J, Amari S, Zinner E K & Lewis R S 1991 Interstellar grains within interstellar grains. Astrophysical Journal Letters 373:L73-L76.

Birck J L & Allègre C J 1984 Chromium isotopic anomalies in Allende refractory inclusions. Geophysical Research Letters 11:943-946.

Black D C & Pepin R O 1969 Trapped neon in meteorites. II. Earth and Planetary Science Letters 6:395-405.

Burbidge E M, Burbidge G R, Fowler W A & Hoyle F 1957 Synthesis of the elements in stars. Reviews of Modern Physics 29:547-650.

Cameron A G W 1962 The formation of the sun and planets. Icarus 1:13-69.

Cameron A G W & Truran J W 1977 The supernova trigger for formation of the solar system. Icarus 30:447-461.

Clayton R N, Grossman L & Mayeda T K 1973 A component of primitive nuclear composition in carbonaceous meteorites. Science 182:485-488.

Clayton R N, Hinton R W & Davis A M 1988 Isotopic variations in the rock-forming elements in meteorites. Philosophical Transactions of the Royal Society of London A325:483-501.

Fahey A J, Goswami J N, McKeegan K D & Zinner E 1985 Evidence for extreme ^{50}Ti enrichments in primitive meteorites. Astrophysical Journal Letters 296:L17-L20.

Fahey A J, Goswami J N, McKeegan K D & Zinner E 1987 ^{16}O excesses in Murchison and Murray hibonites: A case against a late supernova injection origin of isotopic anomalies in O, Mg, Ca, and Ti. Astrophysical Journal Letters 323:L91-L95.

Gray C M & Compston W 1974 Excess ^{26}Mg in the Allende meteorite. Nature: 495-497.

Hartmann D, Woosley S E & El Eid M F 1985 Nucleosynthesis in neutron-rich supernova ejecta. Astrophysical Journal 297:837-845.

Hinton R W, Davis A M & Scatena-Wachel D E 1987 Large negative ^{50}Ti anomalies in refractory inclusions from the Murchison carbonaceous chondrite - evidence for incomplete mixing of neutron-rich supernova ejecta into the solar system. Astrophysical Journal 313:420-428.

Heydegger H R, Foster J J & Compston W 1979 Evidence of a new isotopic anomaly from titanium isotopic ratios in meteoric materials. Nature 278:704-707.

Hoppe P, Amari S, Zinner E, Ireland T & Lewis R 1994 Carbon, nitrogen, magnesium, silicon, and titanium isotopic compositions of single interstellar silicon carbide grains from the Murchison carbonaceous chondrite. Astrophysical Journal 430:870-890.

Huss G R & Lewis R S 1994 Noble gases in presolar diamonds. I. Three distinct components and their implications for diamond origins. Meteoritics 29:791-810.

Hutcheon I D, Huss G R, Fahey A J & Wasserburg G J 1994 Extreme ^{26}Mg and ^{17}O enrichments in an Orgueil corundum: identification of a presolar oxide grain. Astrophysical Journal Letter 425:L97-L100.

Ireland T R 1990 Presolar isotopic and chemical signatures in hibonite-bearing refractory inclusions from the Murchison carbonaceous chondrite. Geochimica et Cosmochimica Acta 54:3219-3237.

Ireland T R 1995 Ion microprobe mass spectrometry: Techniques and applications in cosmochemistry, geochemistry, and geochronology. In: Advances in Analytical Geochemistry Vol II (eds M Hyman & M Rowe). JAI Press, Greenwich, 1-118.

Ireland T R, Compston W & Heydegger H R 1985 Titanium isotopic anomalies in hibonites from the Murchison carbonaceous chondrite. Geochimica et Cosmochimica Acta 49:1989-1993.

Ireland T R, Zinner E K & Amari S 1991 Isotopically anomalous Ti in presolar SiC from the Murchison meteorite. Astrophysical Journal Letters 376:L53-L56.

Ireland T R, Zinner E K, Fahey A J & Esat T M 1992 Evidence for distillation in the formation of HAL and related hibonite inclusions. Geochimica et Cosmochimica Acta 56:2503-2520.

Jungck M H A, Shimamura T & Lugmair G W 1984 Ca isotope variations in Allende. Geochimica et Cosmochimica Acta 48:2651-2658.

Lee T 1988 Implications of isotopic anomalies for nucleosynthesis. In: Meteorites and the Early Solar System (eds J F Kerridge & M S Matthews). University of Arizona Press, Tucson, 1063-1089.

Lee T & Papanastassiou D A 1974 Mg isotopic anomalies in the Allende meteorite and correlation with O and Sr effects. Geophysical Research Letters 1:225-228.

Lee T, Papanastassiou D A & Wasserburg G J 1977 Aluminium-26 in the early solar system: Fossil or fuel? Astrophysical Journal Letters 211:L107-L110.

Lewis R S, Tang M, Wacker J F, Anders E & Steel E 1987 Interstellar diamonds in meteorites. Nature 326:160-162.

Lewis R S, Amari S & Anders E 1994 Interstellar grains in meteorites: II. SiC and its noble gases. Geochimica et Cosmochimica Acta 58:471-494.

Niemeyer S & Lugmair G W 1981 Ubiquitous isotopic anomalies in Ti from normal Allende inclusions. Earth and Planetary Science Letters 53:211-225.

Ott U 1993 Interstellar grains in meteorites. Nature 364:25-33.

Reynolds J H & Turner G 1964 Rare gases in the chondrite Renazzo. Journal of Geophysical Research 69:3263-3281.

Truran J 1993 Interstellar grains in the laboratory. Workshop on Isotopic Anomalies, Washington University, St. Louis, Missouri.

Zinner E K, Fahey A J, Goswami J N, Ireland T R & McKeegan K D 1986 Large ^{48}Ca anomalies are associated with ^{50}Ti anomalies in Murchison and Murray hibonites. Astrophysical Journal Letters 311:L103-L107.

Zinner E, Tang M & Anders E 1987 Large isotopic anomalies of Si, C, N and noble gases in interstellar silicon carbide from the Murray meteorite. Nature 330:730-732.

Zinner E, Tang M & Anders E 1989 Interstellar SiC in the Murchison and Murray meteorites: Isotopic composition of Ne, Xe, Si, C, and N. Geochim. Cosmochim. Acta 53:3273-3290.

Zinner E, Amari S, Anders E & Lewis R 1991a Large amounts of extinct ^{26}Al in interstellar grains from the Murchison carbonaceous chondrite. Nature 349:51-54.

Zinner E, Amari S & Lewis R S 1991b s-Process Ba, Nd, and Sm in presolar SiC from the Murchison meteorite. Astrophysical Journal Letters 382:L47-L50.